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1. Action of Hydrochloric Acid Gas Upon Arsenates and Nitrates.

2. The Atomic Weights of Nitrogen and Arsenic.

Thesis
Presented to the Department of Philosophy of the
University of Pennsylvania,
For the Degree of Doctor of Philosophy.

BY
JOSEPH GILLINGHAM HIBBS, M. S.

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The experiments herein recorded were conducted under the supervision of Dr. Edgar F. Smith, and I hereby most heartily thank him for his valuable suggestions and constant attention during their performance.

J. G. H.

INTRODUCTION.

It has only been in recent years that any degree of attention has been directed to the separation of metals, or their oxides, by the different volatility shown by them when heated in the vapors of hydrochloric acid.

Debray * obtained the exceedingly volatile compound molybdenyl dihydroxy-dichloride ($Mo\ O_2\ (OH)_2\ Cl_2$) when hydrogen chloride was conducted over perfectly dry molybdenum trioxide; but the fact was never utilized in the analytical way until Pechard † and others ‡ made it the basis of a separation of molybdic from tungstic acid. The same idea likewise served for the determination of the atomic weight of molybdenum §, adding a result in every respect comparable with those deduced by other methods.

Vanadic acid || also was found to be completely eliminated from its salts, when the latter, at a gentle heat, were exposed to the action of the acid gas.

The investigations here alluded to have suggested a study of other elements in similar directions. Thus nitrates, arsenates, phosphates and the trioxide of antimony have been drawn into the field of experiment and the results obtained from them constitute an essential portion of the present research.

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* Compt. rendus 46,1098. Liebig's Annalem 108,250.

† Compt. rendus 114,173.

‡ Z. f. anorg. Chemie 4.236.

§ Z. f. anorg. Chemie 4.236.

|| Z. f. anorg. Chemie 7.41.

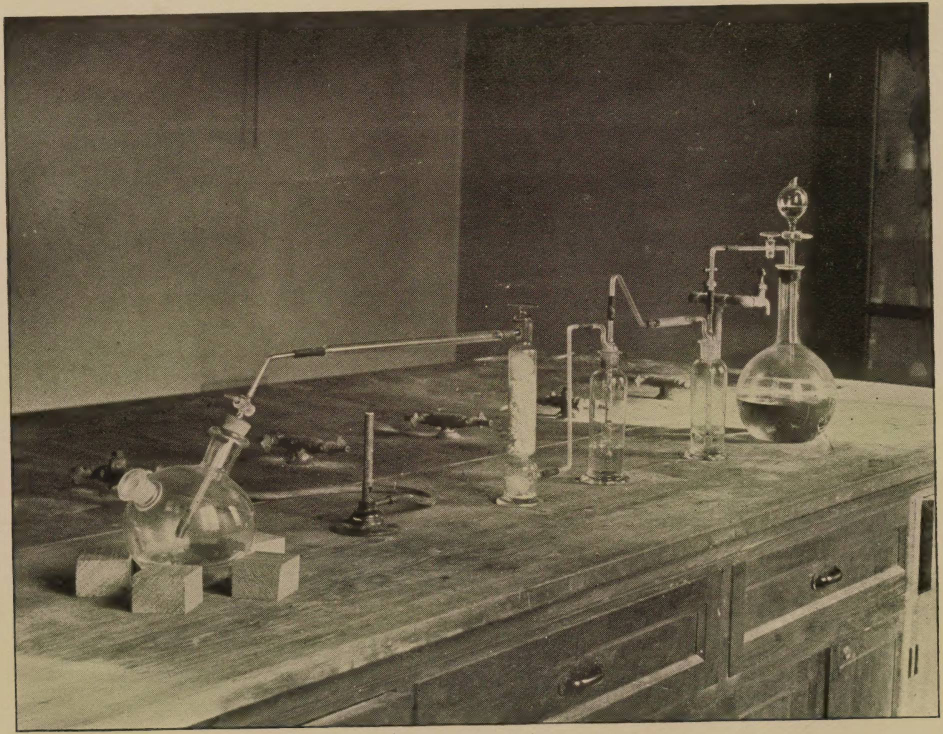
FIRST SECTION.

Care was exercised in the preparation of the hydrochloric gas used in the many determinations and separations which were conducted.

It was evolved from concentrated sulphuric acid and hydrochloric acid and was purified as indicated in the apparatus, a sketch of which is here introduced. The construction of this device is so simple that a glance will suffice for the comprehension of the method used in the experiments recorded later.

The introduction of the sulphuric acid into the muriatic acid was made by means of a separatory funnel. Such a generator needs no special attention, as a constant evolution of gas may be obtained without the application of heat. Any degree of velocity of current of the gas can be procured by decreasing or increasing the flow sulphuric acid. As the gas was evolved, it was passed through an empty wash bottle, from that over moist silver chloride, then through concentrated sulphuric acid and finally through a calcium chloride tower. It was then considered to be sufficiently anhydrous to be conducted through a combustion tube of hard glass, over a boat containing the salt, thence into a receiving bulb provided with a stopcock. The bulb contained about 200 c. c. of distilled water and 10 c. c. of dilute nitric acid.

In performing the experiment with this device the following procedure was observed. The generator was connected with the remaining part of the apparatus, all stopcocks were opened and the entire system charged with the acid gas. When this condition prevailed, the end of the combustion tube was opened, the boat was quickly introduced and the tube again closed. As soon as the action in the boat was



APPARATUS, (SEE PAGE 4).

at an end, the burner was removed from under the combustion tube, and the latter allowed to cool while a current of gas passed through the entire system.

The introduction of the sulphuric acid into the generator was stopped, when the apparatus was thoroughly cooled. At the same time the cocks in the bulb and the calcium chloride tower were turned off to prevent any backward suction from the bulb.

The generator was then removed to a "hood" and any residual gas permitted to escape.

The boat was removed to a vacuum desiccator and allowed to stand at least four hours before taking its weight.

The record of results may now be presented:

A.—Action of Gaseous Hydrochloric Acid upon Sodium Pyroarsenate.

Commercial sodium arsenate was recrystallized until the salt was obtained pure. Well defined crystals were selected and ignited to the pyroarsenate, which was crushed to fineness and dried at 150° C. in a drying bottle for one hour. A weighed portion of this material was placed in a porcelain boat and introduced into the combustion tube. No volatilization took place in the cold; a gentle heat, however, eliminated a whitish vapor, condensing at the anterior end of the tube to a colorless liquid. This, on application of a gentle heat, rapidly vanished from the tube walls as a white smoke, which was rapidly absorbed by the bulb-contents, unless a too strong stream of the gas drove it through the liquid to the surface, where it broke forth as a heavy smoke, which immediately sank to the surface of the liquid and was there absorbed. The length of time to which the salt was exposed to the acid gas depended upon the degree of temperature applied. Thus, at a temperature of 250° C. it was found that fifteen minutes were sufficient; but as a safeguard the action was permitted to continue forty-five minutes.

When the metallic oxide was thus freely expelled by the acid, the boat was allowed to cool and was then weighed, after which its contents were dissolved in water and tested with a "magnesia mixture." A precipitate did not appear, even after standing twenty-four hours.

In the second experiment the boat and contents were introduced into a Marsh's Apparatus, but not the faintest indication of arsenic was detected.

The combustion tube, connecting tube and bulb, together with its original contents, were carefully washed with water into a beaker, a small amount of nitric acid added and the solution brought to boiling, allowed to cool and the arsenic precipitated by a "magnesia mixture." The precipitate that appeared was dissolved in hydrochloric acid, reprecipitated with ammonia, allowed to stand twelve hours, when it was filtered, washed with ammonium hydrate (1-3), dissolved from off the filter with nitric acid, the solution passing into a weighed porcelain crucible; in which it was carefully evaporated to dryness, then gently ignited to expel the ammonium salts and finally weighed.

It is impossible to assert in precisely what form the arsenic was volatilized, but it is probable that both arsenious and arsenic oxides were present in the receiver, as in one trial in which no nitric acid was added to the bulb contents, the resulting magnesium pyroarsenate was light in weight.

A trial was made to ascertain the shortest time possible for the complete elimination of the arsenic. After raising the temperature to about 500° C. it was found that it required thirty seconds to eliminate the metallic oxide from about two tenths of a gram of sodium pyroarsenic.

When the condensed vapor was rapidly heated to a high temperature in the acid gas, the odor of chlorine was noticed coming out from the bulb. Care must be taken in heating the arsenate, as the salt fuses at a comparatively low temperature. As the arsenic is eliminated, the temperature of the boat may be increased, the residual sodium chloride not being so easily fused as the arsenate. The following results were obtained:

	Amount of Arsenate taken.	Pyroarsenate Required.	Pyroarsenate Obtained.
1.	.3844 gr.	.3361 gr.	.3355 gr.
2.	.1093 "	.0956 "	.0959 "

B.—Action of Gaseous Hydrochloric Acid upon Sodium Pyrophosphate.

Pure, recrystallized disodium hydrogen phosphate was ignited to the pyrophosphate and the latter exposed to the acid vapors in the same manner as the corresponding arsenate, but the phosphoric acid was *not* expelled.

No apparent change took place in the boat; the color of the salt remained white and it appeared to be in the same condition as before its introduction into the tube. When the boat was removed and weighed, after having stood several hours in a vacuum desiccator, it exceeded its original weight. Upon heating it in the air an effervescence was observed and the odor of hydochloric acid was noticed; therefore the increase in weight must have been due to absorbed hydrochloric acid gas, which the salt tenaciously held even after long standing.

Attention was next directed to the contents of the bulb. They were removed, a little nitric acid added, and the solution brought to boiling. When cold, ammonium hydrate and "magnesium mixture" were added and the liquid thoroughly stirred. The solution was allowed to stand three days without the formation of a precipitate, hence it was safe to infer that phosphoric acid was not volatilized.

C.—Separation of Arsenic Acid from Phosphoric Acid.

1.—Acids existed as Sodium Salts.

Having ascertained that arsenic acid could be volatilized and that phosphoric acid could not, an attempt was made to separate them by this means. Weighed portions of their sodium salts were mixed and subjected to the action of hydrochloric acid as described in the preceding paragraph. The characteristic arsenic distillation took place; the contents of the boat were dissolved in water, the solution brought to boiling and hydrogen sulphide was passed through it for three hours but no signs of arsenic were observed.

In another experiment the boat and its contents were placed in a Marsh's Apparatus, but not the slightest trace of a mirror was noticed.

The contents and washings of the bulb and its connection were analyzed for their arsenic contents with the following results:

	$Na_4P_2O_7$ Taken.	$Na_4As_2O_7$ Taken.	$Mg_2P_2O_7$ Required.	$Mg_2P_2O_7$ Obtained.	$Mg_2As_2O_7$ Required.	$Mg_2As_2O_7$ Obtained,
1.	1 gr.	1 gr.	.0834 gr.	.0830 gr.	.0874 gr.	0869 gr.
2.	11 "	11 "	.0918 "	.0909 "	.0961 "	.0957 "

C. 2.—Acids existed as Magnesium Salts.

Sodium pyrophosphate and sodium pyroarsenate were separately dissolved in water and each acid precipitated as its magnesium ammonium salt. These salts were then filtered, washed, dried and carefully removed from the filter and ignited, after which they were subjected to the action of gaseous hydrochloric acid. The results were as follows:

	$Mg_2P_2O_7$ Taken.	$Mg_2As_2O_7$ Taken.	$Mg_2P_2O_7$ Obtained.	$Mg_2As_2O_7$ Obtained.
1.	.1100 gr.	.1100 gr.	.1105 gr.	.1094 gr.
2.	.11 "	.11 "	.1108 "	.1091 "

This method of separation of arsenic and phosphoric acid is one in which the error is reduced to a minimum. Then, too, the time necessary for the completion of the experiment is brief indeed, when compared with the long, tedious reduction and precipitation of the arsenic by means of hydrogen sulphide.

It is not absolutely necessary that the salt be anhydrous before its introduction into the combustion tube.

D.—Action of Gaseous Hydrochloric Acid upon Lead Arsenate.

A weighed amount of the lead arsenate, made by precipitation of the sodium salt in water solution by lead acetate, was introduced into a current of gaseous hydrochloric acid. Immediately upon heating the characteristic arsenic volatilization took place, and the boat contents became white in color. If the arsenic had been completely eliminated the salt remaining in the boat should be lead chloride. The following results show such to have been the case:

	$Pb_3(AsO_4)_2$ Taken.	$PbCl_2$ Required.	$PbCl_2$ Obtained.
1.	.2965 gr.	.2747 gr.	.2746 gr.
2.	.3608 "	.3343 "	.3347 "

In each experiment, after weighing, the boat and its contents were placed in a Marsh's Apparatus but no trace of arsenic was observed.

The arsenic solution in the bulb was analyzed and .1028 gr. of magnesium pyroarsenate was found, while .2965 gr., the amount of lead arsenate taken, required .1022 gr. of magnesium pyroarsenate.

The mineral mimetite was found to be as easily decomposed as the simple salt. The following results were obtained:

	Mimetite Taken.	Per ct. Arsenate Obtained.
1.	.2686 gr.	10.42
2.	.3950 "	10.39

In neither experiment did the boat contents give any reaction for arsenic.

E.—Separation of Arsenic Acid from Tungstic Acid.

Smith and Oberholtzer [*] ascertained that tungstic acid was not volatile in a stream of gaseous hydrochloric acid, and as the opposite was true of arsenic acid a probable method of separation for these elements suggested itself.

As tungsten compounds invariably carry a small amount of molybdenum trioxide, it is necessary to subject such a compound to a current of hydrogen chloride in order to eliminate the last traces of molybdic acid.

Sodium tungstate was dried and subjected to the action of the gas; the experiment was unsatisfactory, however, as the salt broke up into sodium chloride and tungsten trioxide; so that pure tungsten trioxide was used. Weighed portions of it and sodium pyroarsenate were thoroughly mixed and subjected to the action of the gas. Extreme care must be taken when heating the boat; although tungsten trioxide is not volatile in any form when subjected to the action of the acid gas, a high temperature will mechanically carry it out of the boat, so a low temperature is imperative.

The characteristic arsenic volatilization occurred and sodium chloride and tungsten trioxide remained in the boat. Several hours' standing in a vacuum desiccator suffices to remove the last traces of the acid gas and the boat may then be safely weighed. Deducting the weight of the boat and unaltered tungsten trioxide gave the weight of sodium chloride. The following are the results:

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[*] Z. f. Anorg. Chemie. 4, 236.

	Taken.	Required.	Obtained.
1.	.1253 gr. WO_3	.0961 gr. NaCl.	.0961 gr. NaCl.
	.1456 " $Na_4As_2O_7$	.1273 " $Mg_2As_2O_7$	.1270 " $Mg_2As_2O_7$
2.	.1127 " WO_3	.1188 " NaCl.	.1189 " NaCl.
	.1800 " $Na_4As_2O_7$	.1574 " $Mg_2As_2O_7$	.1576 " $Mg_2As_2O_7$
3.	.0409 " WO_3	.0709 " NaCl.	.0707 " NaCl.
	.1073 " $Na_4As_2O_7$	.0938 " $Mg_2As_2O_7$	.0935 " $Mg_2As_2O_7$
4.	.0842 " WO_3	.0695 " NaCl.	.0692 " NaCl.
	.1053 " $Na_4As_2O_7$	.0920 " $Mg_2As_2O_7$	.0921 " $Mg_2As_2O_7$
5.	.1427 " WO_3	.0431 " NaCl.	.0433 " NaCl.
	.0653 " $Na_4As_2O_7$	.0568 " $Mg_2As_2O_7$	.0574 " $Mg_2As_2O_7$

F.—Separation of Molybdic Acid from Phosphoric Acid.

Of all the separations attempted by this method, this one proved to be the most difficult. The first and most important condition is that of *absolute* dryness of apparatus, salt and gas. If this precaution is not strictly maintained, a reduction of the molybdenum trioxide will ensue and the separation will prove to be a failure.

When molybdic acid is eliminated from a molybdate this condition of absolute dryness is not so essential, as a high temperature will drive over the lower oxide there formed; but in this instance, the sodium pyrophosphate present will fuse at a comparatively low temperature enclosing some of the molybdenum compound and thus prevent a complete separation.

If, however, absolute dryness is maintained and the boat is heated before its introduction into the combustion tube, the latter being filled with dry air, not with hydrochloric acid gas, and a low temperature being applied, a complete separation can be effected without the formation of the least trace of the blue or green oxide of molybdenum.

In the second place, it will not do to charge the combustion tube with the acid gas before introducing the boat, because the affinity of the hydrochloric acid for moisture is so great that no matter how quickly the introduction should be made, water will show itself in the tube. The only alteration in the apparatus in this experiment was the substitution of a longer combustion tube (one metre) to prevent the entrance of moisture from the bulb. Both sodium molybdate and molybdenum trioxide were used with the following results:

	$Na_4P_2O_7$ Taken.	Na_2MoO_4 Taken.	MoO_3 Taken.	MoO_3 Obtained.
1.	.2327 gr.	.0400 gr.	.0279 gr.	.0281 gr.
2.	.4509 "	.2786 "	.1946 "	.1948 "
3.	.3269 "		.0744 "	.0745 "
4.	.1349 "		.0424 "	.0422 "
5.	.110 "		.0898 "	.0898 "

G.—Action of Gaseous Hydrochloric Acid upon Sodium and Potassium Nitrates.

The purest sodium nitrate obtainable was recrystallized four times, the best crystals selected and thoroughly dried at 210°C. for one hour, after which the mass was finely powdered and again dried in a drying bottle for one hour. On introduction into the gas, action began in the cold; the salt took on a yellowish-brown color and a yellow liquid condensed in the cooler part of the tube.

In about fifteen minutes at a temperature of 300°C. the salt regained its former whiteness of color, which condition continued upon further application of heat. Forty-five minutes were allowed in each experiment to insure the complete elimination of the oxide of nitrogen.

On examination of the boat contents nothing was revealed but sodium chloride. The odor of the bulb contents is that of nitric acid together with disassociated nitrogen dioxide, which latter probably gave the color to the condensed product.

That the elimination was complete is proved by the following results:

The first four experiments were made with sodium nitrate, the fifth with potassium nitrate.

	Weight of substance taken.	NaCl. required.	NaCl. obtained.
1.	.1878 gr.	.1290 gr.	.1289 gr.
2.	.2971 "	.2041 "	.2040 "
3.	.3536 "	.2427 "	.2429 "
4.	.6462 "	.4439 "	.4440 "
	Weight of substance taken	Required KCl.	Obtained KCl.
5.	.2591 gr.	.1908 gr.	.1908 gr.

L.—Action of Gaseous Hydrochloric Acid upon Antimony Trioxide.

Action commences immediately upon the introduction of the oxide into the gas, and it is completed in the cold according to the following equation:

$$Sb_2O_3 + 6\ Hcl = Sb_2Cl_6 + 3\ H_3O.$$

The color of the boat-contents changes from a cream-white to the color of antimonic chloride, most of which is dissolved in the water there formed. Some water vapor and antimonic chloride are mechanically carried over. A gentle heat, however, quickly distils over the water, then the antimonic chloride follows as a light colored smoke, condensing to a yellow liquid in the anterior part of the tube. A film of some insoluble residue was left in the boat, an impurity of the oxide, probably silica, which on testing gave no evidence of antimony.

I.—Action of Gaseous Hydrochloric Acid on Potassium Chromate.

On the introduction of this salt into the gas even in the cold an action sets in, which gradually diminishes until nothing more volatile distils from the boat. On applying heat, the same action is repeated, that is, a yellow liquid of the same color and shade as the salt used condensed from a vapor of the same color at the anterior end of the tube. In about five minutes this action again ceased, similar to the action in the cold. Greater heat was applied, but no further volatilization took place. The color of the boat contents changed from the original yellow to a golden brown, which deepened perceptibly in shade till a deep brown was reached, which, when a high temperature was applied, changed into a deep purple.

No matter how much longer the heat was applied, the contents continued to have the same appearance.

When cold and removed from the combustion tube, the sintered mass showed a green patch on the lower side, probably caused by reduction. The bulb contents gave qualitative reactions for chromium, showing some to have been eliminated by the acid gas; but no condition here tried was suitable for its complete elimination. Further attempts were made with varying conditions in each case, but the results were similar to that above recorded.

SECOND SECTION.

The Atomic Weights of Nitrogen and Arsenic.

In the first section of this investigation mention was made of the fact that the atomic weight of the metal molybdenum had been determined by expelling molybdic acid from sodium molybdate with hydrochloric acid gas, then weighing the residual sodium chloride.

Having found that nitric acid and arsenic acid were driven from their alkali salts with ease, leaving a chloride that was absolutely pure, and believing that the atomic masses of nitrogen and arsenic determined in this manner would afford a valuable contribution to the literature relating to these constants, a carefully conducted series of experiments was made with two nitrates and one arsenate. The results are given in detail in the following lines:

The Atomic Weight of Nitrogen.

In the past, determinations of the atomic weight of nitrogen have been made from the density of the gas itself, from the ratio between ammonium chloride and silver, and from the decomposition of certain nitrates. The first method in particular has been frequently applied. Thomson, Dulong, Berzelius and Lavoisier, brought to light many new facts relating to the atomic weight of nitrogen, unfortunately, however, considerable that they have presented has been affected by complications that have introduced inaccuracies.

Dumas and Boussingault * found the mean density of nitrogen to be .972; for hydrogen they found a mean density of .0693, which would give nitrogen an atomic weight of 14.026. Regnault obtained a more concordant series of results, the mean being .97137, and a density for hydrogen of .0692, which makes the atomic weight of nitrogen equal to 14.0244.

Clark gives in detail his computation of the means of the results obtained by Penny, Stas and Marignac. Their work on the determination of the atomic weight of this particular element was mainly on the ratio of ammonium chloride and silver, and the decomposition of certain nitrates. A great degree of accuracy was maintained throughout the entire investigation; but the amount of work required to obtain a single result, necessarily lays the method open to a serious error of manipulation.

In this connection a paragraph from Clark's "A Recalculation of the Atomic Weights" may be cited: "The general method of working upon these ratios is due to Penny. Applied to the ratio between the chloride and nitrate of potassium, it is as follows: A weighed quantity of the chloride is introduced into a flask which is placed upon its side and connected with a receiver. An excess of pure nitric acid is added, and the transformation is gradually brought about by the aid of heat, the nitrate is brought into a weighable form. The liquid in the receiver is also evaporated, and the trace of solid matter which has been mechanically carried over, is recovered and also taken into account."

The method indicated in this study, and actually applied with the results appended, is decidedly less objectionable. In this method there is no distillation, no precipitate, in fact, nothing that could involve serious error.

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* Comptes Rendus, 1841—12. 1005.

Clark summarizes the results of Penny, Stas and Marignac as follows :

1. From Specific Gravity of N.— N. = 14,0244
2. " Ammonium Chloride— N. = 14,0336
3. " Ratio number four— N. = 14,0330
4. " Silver Nitrate— N. = 13,9840
5. " Potassium Nitrate— N. = 13,9774
6. " Sodium Nitrate— N. = 13,9906

Mean of results for N. = 14,0210.

If oxygen is 16, this becomes 14.0291. Stas found the atomic weight of nitrogen to be 14.044. Dumas found 14. by experiments on the combustion of ammonia and cyanogen (o = 16). Pelouze found 14.014 by bringing a known weight of silver nitrate in contact with a known and slightly excessive weight of ammonium chloride, which excess was titrated. Anderson found 13.95 by the decomposition of the nitrate of lead, with just enough heat for decomposition (the same method that was used by Berzelius). Marignac found 14.02 by dissolving a known weight of silver in nitric acid and then melting and weighing the nitrate found.

A.—Atomic Weight of Nitrogen by Action of Hydrogen Chloride upon Potassium Nitrate.

The purest salt obtainable was dissolved in water, filtered and recrystallized six (6) times, a solution of which was tested for chlorides, sulphates, etc., but no impurity was found. One more crystallization was made and the best crystals were selected. These were washed with distilled water and dried at 210° C. for three hours, powdered and again dried, and finally placed in a weighing bottle. This compound was dried before each experiment. It was also allowed to stand in a balance case one hour before weighing. The same degree of care was exercised in the preparation of the boat for weighing.

The weighing bottle was placed on the scale pan and allowed to stand several minutes in order to regain its normal temperature. After weighing, it was quickly opened and a portion of the salt removed to the boat and again closed and allowed to stand in the balance case for several hours before reweighing. The boat was then introduced into the combustion tube and the gas passed over it. The characteristic action took place. The only difference in the method of procedure adopted here and that described in the first section of this paper, was a longer time being given to complete the action, using a lower temperature, in order to do away with all possibility of fusion of the salt. It was then carefully removed to a vacuum desiccator and allowed to stand over night before weighing. It may be said also that experiments were only conducted on clear days to insure the non-entrance of moisture.

With potassium nitrate, no great variation of amount was taken.

Five determinations were made in this case:

No.	KNO_3 Taken. gr.	KCl. Obtained. gr.	Cor. KNO_3 gr.	Cor. KCl. gr.	Cor. Wt. KNO_3 gr.	Cor. Wt. KCl. gr.	Mol. Wt. KNO_3 Obtained.	At. Wt. N. Obtained.
1.	.11084	.08173	.00006	.00004	.11090	.08177	.101,121	14.011
2.	.14864	.00960	.00007	.00005	.14871	.10965	.101,120	14,010
3.	.21056	.15525	.00011	.00008	.21067	.15533	.101,123	14.013
4.	.23248	.17214	.00012	.00009	.23360	.17223	.101,121	14,011
5.	.24271	.17894	.00013	.00009	.24284	.17903	.101,124	14.014

Atomic Weight of Nitrogen = 14,0118 ± 000472.

The atomic values used in these calculations, were taken from "Table of Atomic Masses," revised by W. F. Clark, in October, 1891.

The figures deduced from these values are, of course, subject to any change made by later revision of atomic masses. It is not so much the exact figure to which attention is called, as to the constancy of result brought forward by this method. The values here used were:

Oxygen = 16. Potassium = 39.11. Chlorine = 35.45.
Sp. Gr. KNO_3 = 2.1. Sp. Gr. KCl = 1.99.

B.—Atomic Weight of Nitrogen by Action of Hydrogen Chloride upon Sodium Nitrate.

The same degree of care and method of procedure were here observed as in Division A. The results are as follows:

No.	$NaNO_3$ Taken. gr.	NaCl. Obtained. gr.	Cor. $NaNO_3$ gr.	Cor. NaCl. gr.	Cor. $NaNO_3$ gr.	Cor. NaCl. gr.	Mol. Wt. $NaNO_3$	At. Wt. N.
1.	.01550	.01066			.01550	.01066	85.061	14.011
2.	.20967	.14419	.00009	.00007	.20976	.14426	85.061	14.011
3.	.26217	.18029	.00012	.00009	.26229	.18038	85.064	14.014
4.	.66610	.45805	.00035	.00024	.66645	.45829	85.064	14.014
5.	.93676	.64422	.00042	.00034	.93718	.64456	85.058	14.008

Atomic Weight of Nitrogen = 14.0116 ± 000741.

Atomic values used were:

Oxygen = 16. Sodium = 23.05. Chlorine = 35.45.
Sp. Gr. NaCl = 2.16. Sp. Gr. $NaNO_3$ = 2.26.

When these results are compared with those obtained by Penny and Stas by treatment of potassium chloride with nitric acid, and the treatment of potassium nitrate with hydrochloric acid (likewise for sodium), a close comparison can be made.

Penny.		Hydrogen Chloride Method.	
For KNO_3	13,9774	For KNO_3	14.0118
" $NaNO_3$	13,9906	" $NaNO_3$	14.0116

Showing a difference of

00.0344 for potassium salt.
00.0210 for sodium salt.

When a mean of the above results is taken, the atomic weight of nitrogen equals

13.9996 for potassium salt.
14.0011 for sodium salt.

Taking now a mean of these values, the atomic weight of nitrogen would be

14.0003.

C.—The Atomic Weight of Arsenic.

The atomic weight of arsenic has been obtained from the chloride ($As\ Cl_3$), the bromide ($As\ Br_3$), and the trioxide (As_2O_3).

Pelouze, in 1845,* and Dumas, in 1859, determined it by the titration with known quantities of pure silver in the analysis of arsenic trichloride. The mean of their results as computed by Clark, gives the atomic weight of arsenic, *74.829*. Wallace † makes the same titration with silver in the analysis of arsenic tribromide. His value is *74.046*. Kessler made a set of determinations by estimating the amount of potassium bichromate required to oxidize one hundred parts of arsenic trioxide to arsenic pentoxide. He obtained a mean value of *75.002*.

A mean of these results gives the following:

From $As\ Cl_3$ — 74.829
" $As\ Br_3$ — 74.046
" As_2O_3 — 75.002
General mean = 74.918.

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*Comptes rendus 20. 1047.
† Philos. Mag. (4) 18. 279.

If oxygen = 16, then the atomic weight of arsenic will = 75.090.

Berzelius, in 1826, heated sulphur and arsenic trioxide together in such a way that sulphur dioxide alone escaped; this method gave *74.840* as the atomic weight of arsenic. But one experiment was made, so that it does not possess much value. In the above method there seems to be a wide variation in the results obtained, the difference between the extreme values is but little less than one unit.

By the hydrogen chloride method, we have but the weighing of the material used in the determination—which must necessarily enter every estimation or analysis—and a single weighing after the action of the acid gas. As in the case of nitrogen, the method seems to be as short and concise as possible.

The method and modus operandi were exactly the same as those used in the determination of the atomic weight of nitrogen.

The sodium chloride obtained was perfectly white in color. In no instance was it fused. After weighing the salt residue, it showed no traces of arsenic, and was readily soluble in cold water without residue. The same conditions of atmosphere were observed.

As the specific gravity of sodium pyroarsenate could not be obtained, it was determined by means of the specific gravity bottle, against chloroform, and was found to be 2.295; while the specific gravity of sodium chloride was taken as 2.16. The atomic values used were:

Oxygen = 16, Sodium = 23.05, Chlorine = 35.45.

The results here obtained, besides being to a great degree constant, compare favorably with those obtained by Pelouze (74.829), and Kessler (75.002).

A coincidence may here be shown by the fact that the mean of these values gives 74.9155, while the hydrogen chloride method gives 74.9158.

In order to give the method a thorough trial, the amounts taken cover a wide range. The smallest amount used was .02176 gr. of sodium pyroarsenate, and the largest 3.22485 gr. It will also be noticed that the variation in result is but .027 for ten determinations.

No.	$Na_4As_2O_7$ Taken. gr.	NaCl. Obtained. gr.	Cor. $Na_4As_2O_7$ gr.	Cor. NaCl. gr.	Cor. $Na_4As_2O_7$ gr.	Cor. NaCl. gr.	Mol. Wt. $Na_4As_2O_7$	At. Wt. Arsenic.
1.	.02176	.01439	.00001	.00000	.02177	.01439	354.008	74.904
2.	.04711	.03114	.00002	.00001	.04713	.03115	350.042	74.921
3.	.05792	.03828	.00003	.00002	.05795	.03830	354.054	74.927
4.	.40780	.26970	.00021	.00011	.40801	.26981	354.002	74.901
5.	.50440	.33028	.00026	.00017	.50466	.33045	354.033	74.916
6.	.77497	.51222	.00041	.00027	.77538	.51249	354.034	74.917
7.	.82853	.54762	.00044	.00029	.82897	.54791	354.034	74.917
8.	1.19068	.78690	.00056	.00041	1.19124	.78731	354.053	74.926
9.	1.67464	1.10681	.00081	.00051	1.67545	1.10732	354.057	74.928
10.	3.22485	2.13168	.00152	.00099	3.22637	2.13267	354.002	74.901

Atomic Weight of Arsenic = 74.9158 ± 00222.

JOHN HARRISON LABORATORY OF CHEMISTRY,
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